OPTIMIZATION OF CARBOXYMETHYLCELLULOSE PRODUCTION FROM ETHERIFICATION CELLULOSE

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VIVA DATE	:	**12 MARCH 2010**

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PROF. DR. AWANG BONO ____________________

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ABSTRACT

OPTIMIZATION OF CARBOXYMETHYLCELLULOSE PRODUCTION FROM ETHERIFICATION CELLULOSE

Carboxymethylcellulose (CMC) is one of the important modified cellulose that widely used as additives in industries. CMC possesses advantageous properties especially their solubility in water, immiscibility in oil and organic solvent which made it acts as multifunction agent. Therefore, they function as stabilizer, thickener, binder and suspension agent in industries such as food and pharmaceutical. Hence, analysis on CMC production process has been studied by researchers in order to enhance the efficiency of the process to achieve specific properties of CMC needed. Most of the analysis were done using One-Factor-At-Time (OFAT) method, which is time consuming and potentially lead to misinterpretation of results due to lack of information on interaction effects likely to occur in chemical reaction. Therefore, statistical and mathematical technique by Response Surface Methodology (RSM) is employed in this research to overcome the limitations especially interactions effects of CMC reaction conditions. Here, the CMC production was carried out by modifying cotton cellulose to CMC through Williamson etherification reaction. The reaction is efficient, inexpensive and easy to handle. Reaction process were studied with respect to Degree of substitution (DS) and reaction efficiency (RE) by varying the reaction conditions; volume ratio of ethanol to isoprophyl alcohol, reaction temperature, reaction time, concentration of sodium hydroxide (NaOH) and sodium monochloroacetate (SMCA). Production process carried out was approved through chemical structure identification using fourier transform infrared spectroscopy (FTIR), substituent distribution measurement using proton nuclear magnetic resonance, rheological behaviour measurement using rotational viscometer. The result of analysis from RSM is comparable with OFAT in term of effect of single factor. Importance of interaction effects on responses were visualized through interaction plots from RSM. The interaction effect of reaction temperature with SMCA and NaOH concentrations are the most significant. Reaction temperature higher than 50^{0}C is required for optimum reaction to occur. RSM regression model on CMC production process suggested a few optimum solutions for maximum DS and RE. RSM model was validated through experiments carried out and the responses are near to the predicted value. The highest DS and RE that obtained with production conducted under investigated conditions are 0.993 and 63.59% respectively. The respective conditions are reaction temperature at 66.06^{0}C, reaction time at 172.20min, SMCA concentration at 13.90g, NaOH concentration at 19.35%w/v and solvent ratio at 0.87v/v.

ABSTRAK

*Karboksimetil selulosa (*CMC) *adalah salah satu selulosa ubahsuai yang penting dengan kegunaannya sebagai aditif dalam industri. CMC mempunyai ciri-ciri penting yang menjadikanya bertindak sebagai multi-fungsi ejen terutama kelarutannya dalam air, tidak saling larut dalam larutan organik dan minyak. Ciri-ciri tersebut merupakan kunci kepada kegunaan CMC dalam industri pembuatan dengan fungsi sebagai penstabil, pemekatan, pengikat dan keupayaan penipisan. Justeru, proses penghasilan CMC telah dikaji oleh penyelidik untuk meningkatkan kecekapannya supaya CMC dengan ciri khusus dapat dihasilkan. Kebanyakan kajian tersebut dijalankan mengguna cara One-Factor-At-Time(OFAT), dimana caranya memerlukan masa yang banyak dan salah tafsir terhadap keputusannya boleh berlaku disebabkan kekurangan maklumat terhadap interaksi antara pembolehubah dalam tindak balas kimia. Jadi, statistik dan matematik teknik seperti Response Surface Methodology(RSM) telah diguna dalam kajian ini untuk mengatasi kekurangan OFAT terutama hubungan antara pembolehubah dalam tindak balas penghasilan CMC. Dalam kajian ini, CMC telah dihasilkan dengan ubahsuai selulosa daripada kapas linter melalui Williamson etherification. Tindak balas karboksimetil ini adalah efisien dalam ekonomi, murah, mudah dikawal dan kurang bertoksik. Dalam tugasan ini, kadar penggantian (DS) dan kecekapan tindak balas (*RE*) bagi penhasilan CMC telah dibelajar dengan parameter tindak balas yang berbeza; suhu dan masa tindak balas, nisbah bagi etanol kepada isopropanol, kepekatan natrium hidroksi (*NaOH) *dan natrium monokloroacetat (*SMCA)*. Proses penghasilan CMC dalam kajian ini telah dikenalpasti betul melalui kumpulan berfungsi identifikasi dengan mengguna* fourier transform infrared spectroscopy *(*FTIR*), taburan pengganti carboksimetil analisis dengan mengguna Nuklear Magnetik Resonance (*NMR*), dan pembelajaran rheologikal terhadap larutan CMC dengan mengguna viscometer. Analisis dari RSM dan OFAT terhadap kesan tunggal pembolehubah adalah hampir sama. Tetapi analisis* RSM menunjukkan *kesan gabungan bagi parameter tindak balas adalah penting untuk menghasil kadar penggantian dan hasilan yang maksimum. Interaksi antara suhu tindak balas dengan kepekatan SMCA dan NaOH adalah paling signifikan. Tindak balas yang optimum memerlukan suhu melebihi* 50^0C*. Beberapa keadaan tindak balas yang optimum telah dicadang oleh regresi model RSM. Esperimen telah dijalani berdasarkan tiga sets keadaan yang dicadang untuk memastikan kesahihan model* RSM*. Keputusannya menunjukkan nilai yang hampir dengan yang dicadang.* DS *yang tertinggi adalah 0.993 dengan* RE *bersamaan 63.59%. Untuk mendapat nilai tersebut, keadaan tindak balas adalah suhu tindak balas bersamaan* 66.43^0C*, masa tindak balas bersamaan 1172.20min, kepekatan SMCA bersamaan 13.90g, kepekatan* NaOH *bersamaan 19.35%w/v dan nisbah bagi etanol kepada isopropanol bersamaan 0.87v/v.*

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LIST OF SYMBOLS AND ABBREVATIONS

AEC	Anion exchange chromatography
AGU	Anhydroglucose Unit
ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BBD	Box-Behnken Design
C-2	Carbon atom at 2nd position
C-3	Carbon atom at 3rd position
C-6	Carbon atom at 6th position
CCD	Central Composite Design
CMC	Carboxymethylcellulose
COO^-	Carboxyl group
D_2O	Distilled water
D_2SO_4	Sulphuric acid
DF	Degree of freedom
DMA	Dimethylsulfoxide
DOE	Design of Experiment
DP	Degree of Polymerization
DS	Degree of Substitution
DS_t	Theoretical Degree of Substitution
F	F value from Fisher test(statistical test)
FTIR	Fourier Transform Infrared Spectroscopy
GPC	Gel Permeation Chromatography
HCl	Hydrochloric acid
HNO_3	Nitric acid
HPLC	High Performance Liquid Chromatography
ISP	Isopropanol
KBr	Potassium Bromide
MCA	Monochloroacetate
MWD	Molecular weight distributions
N	Normality

n	Number of mole
NaOH	Sodium Hydroxide
OFAT	One Factor At Time
OH	Hydroxyl group
r	Reaction rate
R^2	Coefficient of determination
RE	Reaction Efficiency
RSM	Response Surface Methodology
SMCA	Sodium Monochloroacetate
S_N2	Bimolecular nucleophilic substitution
UL	Ultra low
β	Configuration of Carbon atom in AGU

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Cellulose is the abundant natural biopolymer in the world. It can be found in almost every type of plant, ranging from agricultural waste and forest debris. Cellulose possesses outstanding properties such as biodegradable, biocompatible, strong and stable. Due to the above properties it can be used in wide range of industrial application as an additive. However, in some cases it usage in industries is limited because it is not soluble in water.

Therefore, modification is the method to overcome cellulose insolubility properties in order to retain it advantageous. Modification methods that have been developed are mainly based on oxidation, etherification or esterification of cellulose. The reactions modify the structure of cellulose and suitable to the industrial applications. For example, various type of modified cellulose is available in market such as cellulose nitrate, cellulose carbamate, methyl cellulose and carboxymethylcellulose.

Carboxymethylcellulose (CMC) is the most important among others and million tons of it is produce annually. It has gained its position on the market due to its compatibility in industrial usage, easy handling and low toxicity. CMC is the product of etherification reaction. The production process is easy to handle and cost efficient. CMC is one of the important additives in industries such as detergent, food, cosmetics, and pharmaceutical. Because its outstanding properties such as solubility, film formability and ability to suspend.

CMC is cellulose in which the hydroxyl group of anhydroglucose unit is replaced by the carboxymethyl group of monochloroacetate acid or its sodium salt. However, the properties of the resulted product always fluctuating with the conditions and technology employed in manufacturing process. Due to its important and abundant of cellulose sources, plentiful efforts have been made on its production, chemistry, sources, technology and so on. Peak performance for large-scale production of desired CMC required the understanding of the correlations that exist between the modification processes, chemical structure and functional properties of its final products.

Several studies have revealed the importance of effects of carboxymethylation reaction condition on the properties of CMC especially solubility and rheological behavior. The properties are depending on degree of substitution, uniformity of substituent distribution and molecular weight distribution. However, most of research studies (Pushpamalar *et al.*, 2006; Mario *et al.,* 2005; Barai *et al.*, 1996; Zhao *et al.*, 2003) employed the One-Factor-At-Time (OFAT) technique for the carboxymethylation reaction. This technique involved high cost and time consuming. It does not provide the detail investigation of the effects of reaction conditions on final products especially the interaction effects between two factors.

Hence, statistical design is a need to overcome limitations of OFAT technique. Response surface modeling (RSM) is a systematic methodology that applying statistical and mathematical technique in experimentation design. It is a well organized technique to get more insight on chemical factors that affecting the cellulose carboxymethylation. The reaction conditions need to adjust in order to encourage carboxymethylation instead of side reaction to occur. Therefore, it is important to establish the reaction conditions that favor the carboxymethylation reaction. RSM not just visualizes the effect of one factor on the process, it also studies the interaction effects that mostly occur in chemical reaction. It suggests optimum point of carboxymethylation through regression analysis. The CMC product is predictable with RSM regression equation, thus offers new product design in industries.

In this research, works are focus on establish an empirical model to visualize the relationship between carboxymethylation reaction and CMC characteristic. The visualization guides the determination of the optimal operating condition to produce higher quality of CMC with wide range of application.

Therefore, systematic investigation of CMC production process through RSM is gaining importance in the industry. The applied research methodology will be helpful to produce CMC from different kind of sources.

1.2 RESEARCH OBJECTIVES

The objectives of this research are as stated below:

1. To synthesize carboxymethylcellulose from cotton cellulose.
2. To visualize the effect of carboxymethylation reaction condition on degree of substitution and reaction efficiency using response surface methodology
3. To compare with the conventional One-Factor-At-Time technique.
4. To optimize the carboxymethylation reaction using regression equation from the response surface methodology.

1.3 SCOPE OF RESEARCH

Based on the research objectives mentioned above, the scope of this research can be categorized as:

1. Synthesizing and characterization of carboxymethylcellulose from cotton cellulose. CMC is produce in batch reactor under Williamson's etherification reaction. The product is characterization using Fourier-Transform-Infrared (FTIR) spectroscopy, Nuclear Magnetic Resonance (NMR) and viscometer.
2. To visualize the one factor effect and the interaction effect of carboxymethylation reaction conditions on cellulose using response surface methodology. The result of analysis is compare with One-Factor-At-Time technique for reliability of RSM analysis. The corresponding parameters are:
   - (i) Reaction temperature
   - (ii) Reaction time
   - (iii) Alkylation
   - (iv) Etherification
   - (v) Reaction medium composition

3. To optimize the carboxymethylation reaction on cellulose using response surface modeling with respect to:
   (vi) Degree of substitution (DS)
   (vii) Reaction efficiency (%RE)
4. To approach the kinetic study on carboxymethylation using regression equation from response surface methodology. The corresponding studies will compare with the OFAT method for reliability and feasibility.

1.4 ORGANIZATION OF THE THESIS

The objectives of thesis are organized in three parts:

(i) To understand the chemical parameter effect on carboxymethylation process
(ii) To synthesize and characterize the carboxymethylcellulose
(iii) To design and optimize the reaction condition using response surface methodology

They are systematized into five chapters; introduction, literature review, methodology, result and discussion and conclusion.

First chapter briefly describes the CMC, its synthesize technique, use of response surface methodology in CMC production process and objective of this research.

Chapter two is a literature review on fundamental knowledge on cellulose, CMC properties and characteristics, its synthesize technique, and response surface methodology. This chapter begins with the review on the chemistry on cellulose and importance of investigated product, CMC. The following description including the synthesize technique, characterization, properties and application of CMC product. The influences of CMC preparing conditions are elaborated and the response surface methodology method is basically described.

Chapter three is an experimental process part, extracted from literature review, which describes the CMC synthesize technique and analysis applied. The procedure of RSM technique to study CMC production process is described in this chapter.

The fourth chapter discusses on the obtained experimental data. In this chapter, the identification of produced products is firstly describes. The RSM produce data is interprets; by emphasized on one factor effect and interaction effect of preparing conditions on CMC properties, and the obtained results are compared with previous works that using OFAT method. The optimization of CMC production process using RSM is describes.

The finding on this research is concluded in chapter five based on the discussion in chapter four.